

Вуглецеві наноцибулини в композитах: властивості і застосування

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Маленькі вуглецеві наноцибулини (CNO) – це сферичні багатопшарові структури, що складаються з 6-8 фуллунового ядра, яке оточене концентричними вуглецевими шарами щораз більшого діаметру. У зв'язку з добрими структурними, механічними і електронними властивостями, CNO мають потенційне застосування як композитні матеріали, матеріали стійкі до зношування, магнітні носії, оптичні обмежувачі, сонячні елементи, електроди для паливних елементів або автоемісійні катоди

Усі вуглецеві наноматеріали, у тому числі наноцибулини, мають великі перспективи використання як підсилюючі фази в композитних структурах, зокрема у поєднанні з полімерами. Поліелектроліти, як наприклад полі(діалілдиметиламоній) (PDDA) або хітозан (CHIT) утворюють з вуглецевими наноцибулинами полімерно-наноструктурну матрицю, яка посилює властивості обох компонентів.

Приготування і електрохімічні властивості композиту, виготовленого з CNO та PDDA або CHIT досліджувалися методом циклічної вольтаметрії та електрохімічної імпедансної спектроскопії. Композитні оболонки на поверхнях скляних вуглецевих електродів відкладалися методом нанесення покриття, застосовуючи краплю розчину з вмістом суспендованого CNO та наповнювача, PDDA або CHIT. Тверді оболонки композитів є механічно і електрохімічно стабільними і показують кращі властивості ємнісного опору, ніж чисті CNO. Вони виявляють типову ємнісну поведінку з широкими межами напруги від +600 - 600 мВ.

Поверхня електрода, модифікована в такий спосіб проявляє багато потенційних застосувань. Позитивно заряджені структури композитів PDDA/CNO і CHIT/CNO, пов'язані з присутністю заповнювача, дозволяють притягувати негативно заряджені субстрати. З другого боку, велика група хімічних агентів, зокрема протеїни, показують адсорбційну спорідненість з вуглецевим компонентом. Це робить можливим здійснювати симультанне випробування різних субстанцій, навіть з протилежним зарядом.

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Carbon nano-onions in composites: properties and application

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A novel type of a composite made of small carbon nano-onions (CNOs) with poly(diallyldimethylammonium chloride) (PDDA) or chitosan (CHIT) was prepared and its electrochemical properties were investigated by cyclic voltammetry and electrochemical impedance spectroscopy. Solid composite films were prepared on the glassy carbon electrode surface by solvent evaporation from drop of solution containing CNOs with the filler (PDDA or CHIT). They form relatively porous structures, which exhibit typical capacitive behaviour, as well as excellent mechanical and electrochemical stability over a wide potential window. Better properties of the PDDA/CNOs and CHIT/CNOs composites in comparison with pure CNOs are hoped to allow them to be used in electrochemical sensing. Electrochemical properties of PDDA/CNOs film in PBS solution were examined and their ability to dopamine determination was verified. The composite can be applied not only to determination of a dopamine in a presence of ascorbic acid (AA) and uric acid (UA), but also let for simultaneous assays for all three biomolecules in the same solution.

Keywords – carbon nano-onions, polyelectrolytes, composites, dopamine, electrochemical sensing

1. Introduction

Carbon materials such as fullerenes, nanotubes, nano-onions, nanofibers or nanohorns are commonly known structures, which have generated interest in many areas of science due to their structural, mechanical and electronic properties [1-3].

Carbon nano-onions (CNOs) are spherical structures consisted of a hollow fullerene core surrounded by concentric and curved graphene layers [4-5]. The small ones CNOs (6-8 shells) show higher reactivity and solubility in many solvents than other carbon structures. These advantages derive from roundness shape, multilayer construction, small size and defects on the outer layer of CNOs [6]. Beside this CNOs exhibit good structural, mechanical and electronic properties, what is connect with their potential applications as composite materials, wear-resistant materials or electrodes [7-8]. Additionally easy surface functionalization and non-cytotoxicity give a spectrum of possibilities to use CNOs in sensing and biosensing [9].

Composites containing carbon structures could be useful in determination of many substances. The very good relation in composites is between polymers and

carbon structures, because of both sides relative benefits [10].

Carbon nanotubes are often incorporated into layers of poly(diallyldimethylammonium chloride) (PDDA) and chitosan (CHIT) [11-12]. Both materials are positively charged polyelectrolytes which can bind negatively charged ions from the supporting electrolyte in solution [13]. Therefore they exhibit ionic conductivity and provide an ionic environment for carbon nanomaterials. Composites of carbon nanotubes with PDDA and CHIT have been used mainly in the biosensor [12].

The preparation and electrochemical properties of composite made of CNOs and poly(diallyldimethylammonium chloride) (PDDA) or chitosan (CHIT) were investigated. Positively charged film of PDDA/CNOs composite on the electrode surface was used for electrochemical sensing of dopamine (DA), in the presence of ascorbic (AA) and uric acids (UA).

II. Materials and methods

All used chemicals and solvents were commercially available and used without further purification: chitosan (low-viscous, Fluka), poly(diallyldimethylammonium chloride) solution (PDDA, average $M_w < 100\,000$, 35 wt% in water, Aldrich), sulfuric acid (min 95%, Poch S.A., Poland), phosphate buffer saline (PBS, pH 7.4, Sigma), uric acid (minimum 99%, Sigma), dopamine hydrochloride (3-hydroxytyramine hydrochloride, Sigma), L-ascorbic acid (99+% A.C.S., Sigma-Aldrich). Small-CNOs were obtained by annealing nanodiamond powder (5 nm average particle size) under a positive pressure of helium at 1650°C for 1 hour.

Voltammetric experiments were performed using a potentiostat/galvanostat model 283 (EG&G Instruments) with a three-electrode cell. Electrochemical impedance spectroscopy measurements were performed on an AUTOLAB (Utrecht, The Netherlands) computerized electrochemistry system equipped with the PGSTAT 12 potentiostat and FRA response analyzer expansion cards with a three-electrode cell. The AUTOLAB system was controlled with the GPES[®]4.9 software of the same manufacturer. A glassy carbon disc (GCE) (diameter 1.6 mm) was used as the working electrode, a counter electrode was made from platinum mesh (0.25 mm), and a silver wire was immersed in 0.1 M AgCl and separated from the working electrode by a ceramic tip served as the reference electrode. The studied films were imaged by secondary electron SEM with the use of the S-3000N scanning electron microscope from Hitachi (Tokyo, Japan). The accelerating voltage of the electron beam was either 10 or 20 keV and the working distance was 5 mm.

III. Results and discussion

The results of SEM studies of CHIT/CNOs and PDDA/CNOs films are shown in Fig. 1. The morphology of the composites differs significantly from the morphology of thin films formed only by the fillers. At the micrometre scale, both CHIT and PDDA form smooth and uniform layers on the gold surface (Figs. 1a and 1d,

respectively). The presence of CNOs results in the decrease of surface homogeneity. Both composites exhibit porous morphologies with many channels and outcroppings. The roughness of the composite surface decreases with an increasing amount of CHIT and PDDA in the deposit material.

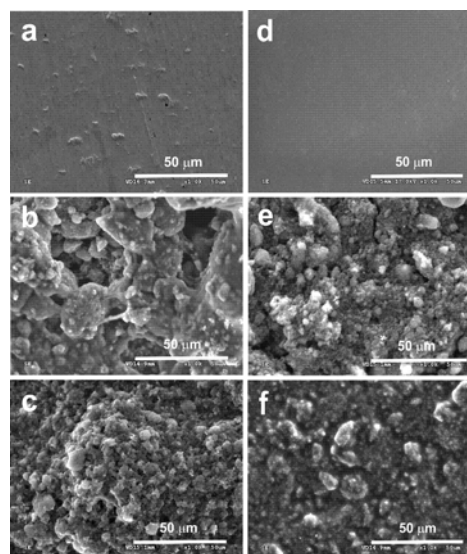


Fig. 1. SEM images of the Au foil covered with (a) CHIT, (b) CHIT/CNOs (1.5:1 mass ratio), (c) CHIT/CNOs (6.5:1 mass ratio), (d) PDDA, (e) PDDA/CNOs (1:1 mass ratio), (f) PDDA/CNOs (4.5:1 mass ratio)

Fig. 2 shows a comparison of the electrochemical properties of CHIT/CNOs (Fig. 2a), and PDDA/CNOs (Fig. 2b) films. In both cases, the amount of the CNOs in the film was the same. All films exhibit typical capacitance behaviour. The voltammograms show almost pseudo-rectangular cathodic and anodic profiles, the characteristic behaviour of an ideal capacitor. Moreover, multiscan CV curves for these films are stable. The potential can be cycled between +600 and -600 mV without any noticeable change in the shape of the voltammogram.

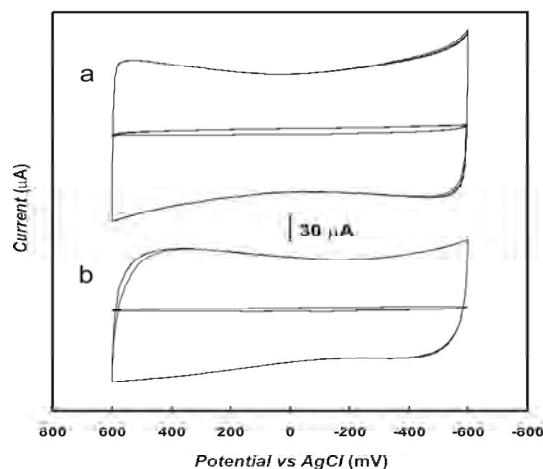


Fig. 2. Cyclic voltammograms of GCE (1.6 mm diameter) covered with (a) CHIT/CNOs (1.5:1) and (b) PDDA/CNOs (1:1) in 0.1 M H_2SO_4 . The sweep rate of 100mV/s

Electrochemical impedance spectroscopy (EIS) was also employed to study the redox properties of the CHIT/CNOs and PDDA/CNOs films. Fig. 3 shows the EIS results obtained for different film compositions of both composites. The impedance spectra of both materials display the expected shape for the double-layer charging porous electrodes.

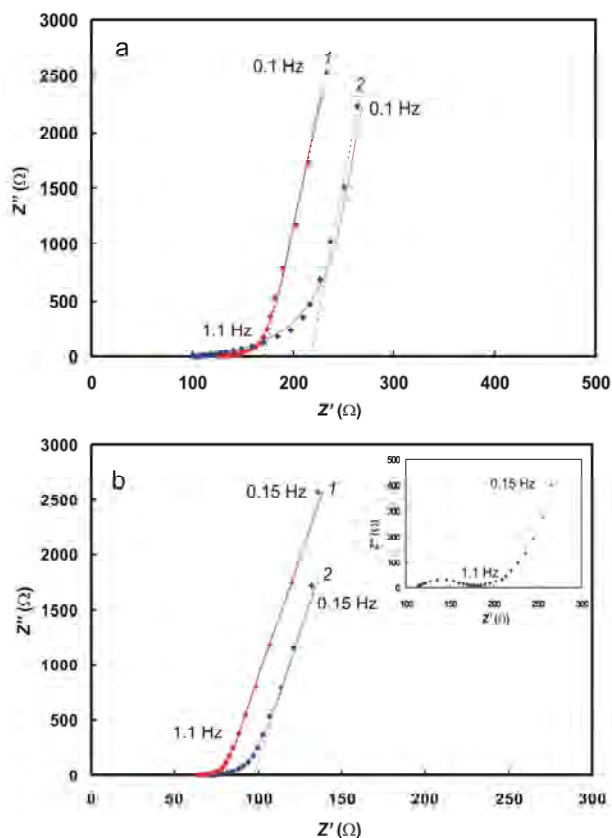


Fig. 3. (a) Complex-plane impedance plots for GCE covered with (1) CHIT/CNOs (1.5:1) and (2) CHIT/CNOs (6.5:1) in 0.1 M H_2SO_4 at 200 mV. (b) Complex-plane impedance plots for GCE covered with (1) PDDA/CNOs (1:1) and (2) PDDA/CNOs (4.5:1) in 0.1 M H_2SO_4 at 600 mV. Frequency was in the range of 10 kHz to 100 mHz. Solid curves represent simulated data. The inset in panel b shows plot obtained for thicker 50 μ m PDDA/CNOs (4.5:1) film

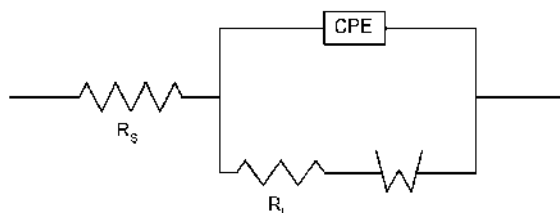


Fig. 4. Equivalent electrical circuit representing behaviour of the CHIT/CNOs and PDDA/CNOs film electrode in an electrolyte solution

The $Z'-Z''$ spectrum exhibits diffusion-controlled behaviour at the higher frequencies, which represents diffusion processes of the counterions in the polymer mass, and capacitive behaviour at the low frequencies. The cross-over between these two domains occurs at about 1 Hz for the CHIT/CNOs and at 2.5 Hz for

PDDA/CNOs. At high frequencies a small loop in the Nyquist plot is seen and this effect is more pronounced for the thicker films (inset Fig. 3b). This loop can be attributed to the contact resistance between the electrode and the current collector in the composite.

Therefore, the equivalent circuit shown in Fig. 4 was proposed to describe the electrochemical behaviour of CHIT/CNOs and PDDA/CNOs composites. This equivalent circuit consists of a solution resistance (R_s), a constant phase element (CPE), that represents the double-layer capacitance (C_{dl}) connected in parallel to the resistance at the electrode/composite interface (R_{ct}), and the Warburg impedance (W). The Warburg impedance represents a transport of counterions through the film during its charging.

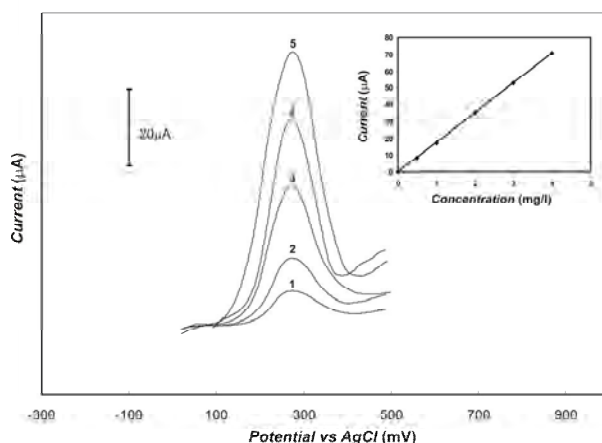


Fig. 5. (a) Determination of DA different concentrations: (1) 0.5, (2) 1, (3) 2, (4) 3, (5) 4 mM by DPV methods on PDDA(0.5% wt. CNOs (3 mg/ml) modified GCE in 0.01 M PBS solution. (Inset: corresponding calibration). Parameters: E : 0.004 V; Amplitude: 0.05 V; Pulse width: 0.05 s; Pulse period: 0.2 s

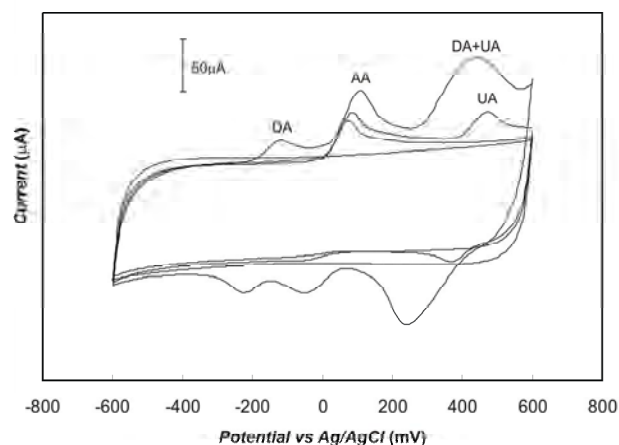


Fig. 6. Determination of 3 mM: DA, AA, and UA by cyclic voltammetry method on PDDA(0.5% wt. CNOs (3 mg/ml) modified GCE in 0.01 M PBS solution. The sweep rate was 100 mV/s

Electrode surface modified in such way demonstrates many potential applications in sensing. The electrochemical determination of dopamine (DA) in the presence of

ascorbic and uric acids (AA and UA) on the PDDA/CNOs modified electrode on the PDDA/CNOs modified electrode were performed. In order to examine the voltammetric determination of the PDDA/CNOs composites to dopamine, we have performed the detection of the different concentrations of the analyte. Since the charging current contribution to the background current is a limiting factor in the analytical determination of electroactive species, experiment was performed using the differential pulse voltammetry (DPV). The oxidation peak current was measured in a 0.01 M pH = 7.4 PBS solution, and plotted against the bulk concentration of DA after background subtraction (Fig. 5). According to the calibration curve (Inset Fig. 5), the dependence of the peak current on the concentration of DA is in a linear relationship in the range of $5 \cdot 10^{-6}$ - $3 \cdot 10^{-3}$ M.

The electrochemical determination of a dopamine in the biological samples causes problems connected with the presence of ascorbic and uric acids usually in large excess compared to the dopamine concentration. At unmodified electrode surface three compounds are oxidized at almost the same potential. The oxidation of AA, DA, and UA at the PDDA/CNOs composite electrode, are observed at 110, 380, and 510 mV vs Ag/AgCl, respectively (Fig. 6), what gives sufficiently good peaks separation. The separation of DA and AA analytical signals is based on electrostatic attraction of negatively charged AA to the positively charged composites (PDDA), which lead to the large negative shift to the voltammetric peak. The oxidation process of UA is almost in the same range as DA, and overlapped it.

Conclusion

PDDA/CNOs and CHIT/CNOs films show better mechanical and capacitance properties than pure CNOs. Therefore, they are promising materials for charge storage applications and ongoing studies will explore these and other properties of these composites.

A novel PDDA/CNOs composite was used for a selective determination of DA with the coexistence of AA and UA. Electrochemical sensing was investigated by cyclic voltammetry and DPV methods. The resulting PDDA/CNOs possessed a faster adsorption dynamics and higher selectivity for DA than the non-modified electrode.

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